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毛萼香茶菜中的新二萜化合物——毛萼晶 P

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摘要 从毛萼香茶菜(*Isodon eriocalyx*)的叶的甲醇提取物中分离得到两个二萜化合物，coetsoidin A 和毛萼晶 P，它们是目前从香茶菜属植物中分离到的仅有的两个 B 环具有 α,β-不饱和酮结构的对映-贝壳杉烷型二萜化合物，其中毛萼晶 P 为新化合物。

关键词 唇形科，毛萼香茶菜，二萜，毛萼晶 P

A NOVEL DITERPENOID FROM ISODON ERIOCALYX

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Abstract From the dried leaves of *I. eriocalyx*, one new *net*-kaurane diterpenoid named maoecrystal P and a known compound coetsoidin A were isolated. They have been the only two *ent*-kaurane diterpenoids possessing α,β-unsaturated ketone functional group in ring B isolated from *Isodon* genus plants so far.

Key words Labiatae, *Isodon eriocalyx*, Diterpenoid, Maoeerystal P

Isodon eriocalyx(Dunn) Hara, a perennial herb or shrub of Labiatae family, has long been used as folk medicine to cure sore throat, inflammation and interdigital disease(中国科学院中国植物志编辑委员会，1997).

One new *ent*-kaurane diterpenoid named maoecrystal P and a known compound coetsoidin A were isolated from the dried leaves of *I. eriocalyx* collected in Jiangchuan County, Yunnan Province.

Coetsoidin A(1)(Wang *et al*, 1989) was the first example of *ent*-kaurane diterpenoid possessing α,β-unsaturated ketone functional group in ring B isolated from *Isodon* genus plants, Its structure was established unambiguously by spectroscopic and X-ray diffraction analysis. Coetsoidin A(1) was also obtained from *Isodon ericalyx* (Dunn) Hara by us. The ^{1}H NMR and ^{13}C NMR data of 1 were consistent with those of the reported one. But the careful study of the assignment of carbon and proton signals in literature revealed that there was something wrong with the assignment at C-5,6,9 and 13 positions. This was proved by 2D NMR spectra. In the ^{1}H-^{13}C COSY spectrum of 1, the proton signals ascribable to H-9β(δ3.72) and H-13α(δ2.66), both of which were determined by ^{1}H-^{1}H COSY spectrum, showed correlation spots with C-9(δ28.0) and C-13(δ41.6), respectively. Thus, the carbon signal attributed to C-9(δ41.6)and C-13(δ28.0) in literature should be interchanged. Moreover, among the long-range couplings observed

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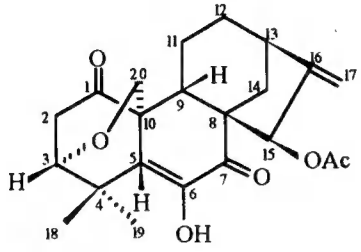
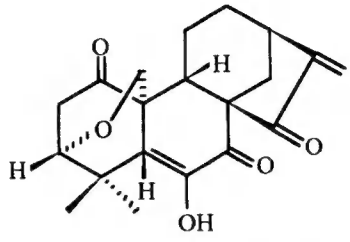
in the COLOC spectrum, the proton signal at H−3, Me−18 and Me−19 showed significant correlations with C−5(δ133.1) respectively. So the signals originally attributed to C−6(δ133.1) and C−5(δ146.1) also should be interchanged. The revised assignment of ^{13}C NMR data were listed in Table 1.



Coetsoidin A (1)



Maoecrystal P (2)

Table 1 ^{13}C NMR data of compounds 1 and 2 in C_5D_5N

(100 MHz, δ with reference to the signal of C_5D_5N)

Carbon	1	2	Carbon	1	2	Carbon	1	2
1	206.2 s	205.4 s	9	28.0 d	32.6 d	17	108.5 t	116.0 t
2	42.0 t	41.9 t	10	53.9 s	54.9 s	18	23.6 q	23.4 q
3	77.9 d	78.0 d	11	19.7 t	19.6 t	19	21.9 q	22.0 q
4	40.8 s	40.9 s	12	32.1 t	30.8 t	20	67.4 t	66.9 t
5	133.1 s	133.4 s	13	41.6 d	38.0 d	OAc	170.5 s	
6	146.1 s	147.0 s	14	38.1 t	38.1 t		20.7 q	
7	194.4 s	192.9 s	15	76.4 d	203.4 s			
8	54.4 s	59.7 s	16	152.5 s	149.0 s			

Table 2 ^{1}H NMR data of compounds 1 and 2 in C_5D_5N

(400 MHz, δ with reference to the signal of C_5D_5N,J in Hz, *overlap)

proton	1	2	proton	1	2
2α	3.03(dd,3.2,19.2)	2.93(dd,3.2,19.6)	14β	1.54(dd,12.0,4.8)	1.98(dd,11.6,4.8)
2β	2.89(dd,3.2,19.2)	2.85(dd,3.2,19.6)	15α	6.83(t,2.0)	
3β	3.86(br.s)	3.84(t,3.2)	17Hb	5.02(bs.s)	6.09(br.s)
9β	3.72(d,7.6)	3.48(d,8.0)	17Ha	5.24(br.s)	5.23(br.s)
11α	1.43～1.47(m,*)	1.42～1.50(m,*)	18Me	1.80(s)	1.78(s)
11β	2.19(m)	1.71(m)	19Me	1.30(s)	1.29(s)
12α	1.28(m)	1.42～1.50(m,*)	20b	4.36(d,8.8)	4.75(d,8.8)
12α	1.43～1.47(m,*)	1.42～1.50(m,*)	20a	4.47(d,8.8)	4.33(d,8.8)
13α	2.66(br.s)	2.95(br.s)	OAc	1.96(s)	
14α	1.80(d,12.0)	2.12(d,11.6)	OH−6	11.00(s)	11.25(s)

Maoecrystal P(2) had a molecular formula of $C_{20}H_{22}O_5$ concluded from the HR EIMS(342.1465[M]$^+$, calc. 342.1467), mp 234.0～236.0℃, $[\alpha]_D^{25}$−141.7 ° (CH_3Cl, c0.30).

A comparison of the ^{1}H and ^{13}C NMR spectral data of 2 with those of 1 indicated that 2 was quite similar to 1 except for ring D. The carbon signal assigned to C−15 at δ76.4 in 1 was replaced by a ketonic signal at δ203.4 in 2 and the proton signal ascribable to H−15αat δ6.83 (1H, t, J = 2.0 Hz) in 1 was disappeared in

2. Meanwhile, the signals assigned to acetyl group in 1 were also absent in 2. All these facts revealed that the structure of 2 was 6-hydroxy-3α, 20-epoxy-*ent*-kaura-5,16-diene-1,7,15-trione.

Compound 2 was the second instance of *ent*-kaurane diterpenoid possessing α,β-unsaturated ketone functional group in ring B isolated from *Isodon* genus plants so far.

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